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REACTIONS OF FREE RADICALS

Final report of Grant DA-ARO-D-31-124-G730,
G355, G373

August 28, 1969
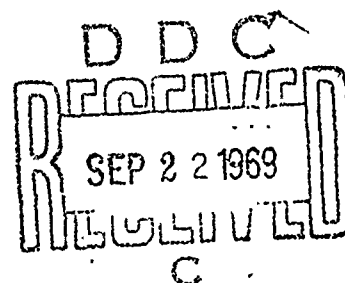
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Abstract

Results of research on the cleavage of triptycene and quinolizinium ions by alkali metals, and on the decomposition of substituted benzoyl peroxides and of cumyl peracetate are reported briefly.

The esr spectra of a series of triarylboron anion radicals show selective line broadening effects. The cleavage of triphenylboron by alkali metals in DME has been shown to give biphenyl in which both moieties of the biphenyl came from the same triphenylboron molecule. Several reactions of diarylboron derivatives with alkali metals are also discussed.

Part I.   Publication List

J.E. Leffler, E. Dolan and T. Tanigaki, J. Am. Chem. Soc., 87, 927 (1965), "Aryl Boron Free Radicals"

M.M. Schwartz and J.E. Leffler, J. Am. Chem. Soc., 90, 1368 (1968), "Behavior of a Sigma Radical with a Peroxide Functional Group."

J.E. Leffler and H.H. Gibson, Jr., J. Am. Chem. Soc., 90, 4117 (1968), "The Radical-Induced Decomposition of Azides."

Part II.   Participating Scientific Personnel

Dr. Teiichi Tanigaki

H.H. Gibson, Jr. (Received Ph.D. August 1967)

Dr. E. Dolan

F.E. Scrivener (Candidate for Ph.D. 1969)

Dr. B.C. Menon

R.E. Schwerzel (Candidate for Ph.D.)

Dr. G. Watts

M.M. Schwartz (Received M.S. Dec. 1967, Candidate for Ph.D.)

D. Miller (Received M.S. 1969)

Part III.   Unpublished Results

A.   The Triptycene Anion Radical (B.C. Menon)

Attempted preparation of the triptycene anion radical from triptycene gave only 9-phenylanthracene, identified by its e.s.r. spectrum. This result will not be published in view of parallel work by T.D. Walsh and R.T. Ross, Tetrahedron Letters, 3123 (1968).

B.   Radicals Derived from Quinolzinium and Related Compounds. (R.E. Schwerzel)

Attempted preparation of the radical I and related species with extended aromatic systems gave only broad esr signals or signals derived from cleavage products. This work may be submitted for

publication as a brief note concerning the direction
of the cleavage reactions.
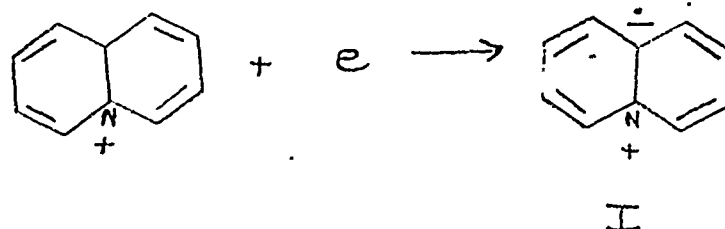
C. Photochemical Carboxy-Inversion Reactions (F.E. Scrivener)

Several unsymmetrically substituted benzoyl
peroxides were photolyzed and found to give sub-
stantially complete radical rather than ion-pair
reaction. See also C. Walling and M.J. Gibian,
J.Am. Chem. Soc., 87, 3413 (1964).

D. Decomposition of Cumyl Peracetate (F.E. Scrivener)

This work, supported in part by ARO, will be
presented for publication later this year after F.E.S.
has put the finishing touches on his dissertation.
Cumyl peracetate was shown to undergo ionic, free-
radical and induced radical decomposition. The ionic
decomposition is catalyzed by acids and by I_2, which
also acts as an inhibitor for the radical-induced
decomposition.

E. Organoboron Radicals (G. Watts, Teiichi Tanigaki,
E. Dolan, D.S. Miller)

Most triarylboron compounds react with alkali
metals in DME to give anion-radicals with an e.s.r.
spectrum showing a characteristic boron splitting
and in most cases a resolved proton hyperfine
splitting.

In the case of trimesitylboron anion radical
in DME or liquid ammonia[1] the characteristic esr
spectrum persists indefinitely, but for other com-
pounds it is succeeded by the spectra of decomposi-
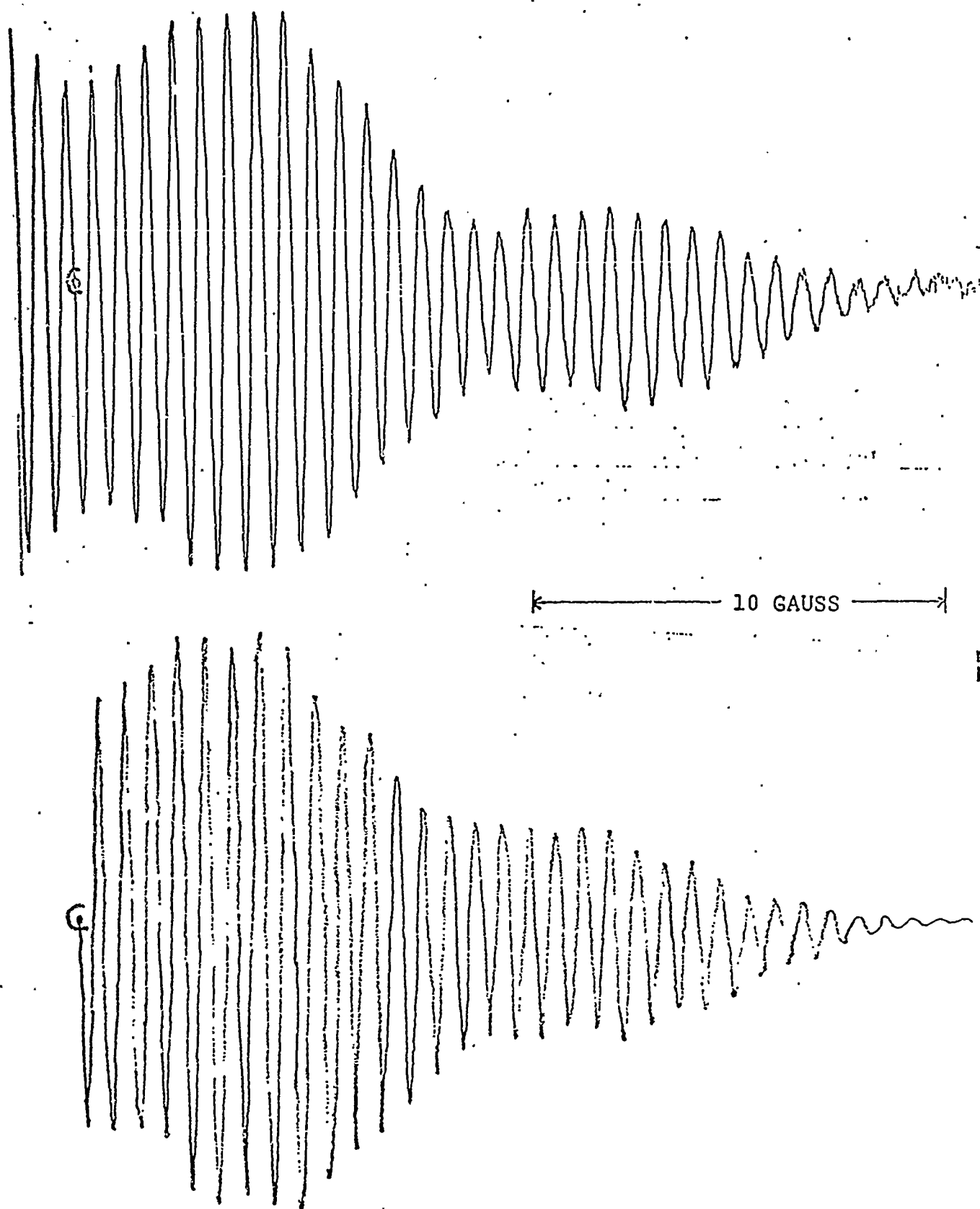tion products, to be discussed in a later section.[2]

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Figure 1. Top: ESR first derivative spectrum of Φ_3B^- generated from Φ_3B and Li in DME. The use of Na/K alloy gives the same spectrum.
Bottom: calculated (first order) spectrum based on $a_B = 7.84$, $a_{O-H} = 1.99$, $a_{m-H} = .675$, $a_{p-H} = 2.70$ and using greater line-widths for the $\pm^3/_2$ boron m_I values than for the $\pm^1/_2$ boron m_I values.

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Triphenylboron Anion Radical

The esr spectrum of triphenylboron anion radical consists of about 63 degenerate lines partly separated by the boron 3/2 spin into four groups. The splitting factors are a_B = 7.86 gauss, a_{p-H} = 2.70 gauss, a_{O-H} = 1.99 gauss, and a_{M-H} = 0.675 gauss. No gegenion splitting was detectable. The four main groups are the result of the splitting by the ^{11}B isotope of spin 3/2. The outer groups corresponding to $\widehat{m}_B$ = +3/2 are only about 40% as intense as the $\widetilde{m}_B$ = +1/2 lines in the derivative spectrum as a consequence of selective line broadening. The high-field half of the spectrum is also slightly less intense than the low-field half; the $\overline{m}_B$ = +1/2 lines are about 85-90% as intense as the $\widehat{m}_B$ = -1/2 lines, with a similar ratio for the $\overrightarrow{m}_B$ = ±3/2 lines.

The spectrum of trimesitylboron anion radical shows similar but much smaller line broadening effects; the $\overrightarrow{m}_B$ = +3/2 derivative amplitudes are about 70% of the $\widetilde{m}_B$ = +1/2 amplitudes. The $\widetilde{m}_B$ = +1/2 derivative amplitudes are equal within experimental error to those of the $\widehat{m}_B$ = -1/2 lines. The hyperfine structure seems to be slightly more resolved on the high field side of the spectrum.

The assignment of splitting factors to the various ring positions and the validity of a model with three equivalent rings was tested by selective deuteration and computer plots[3] of the spectra of both the perhydro and deuterated species. The deuterated species were tris(p-deuterophenyl)boron and tris(3,5-dideuterophenyl)boron and perdeutero-triphenylboron.

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Fairly good fits to the experimental spectra were obtained using the boron and proton splitting constants cited above and the corresponding deuteron splitting constants. The variation in derivative amplitude between the $\widehat{m}_B$ = +1/2 and $\widehat{m}_B$ = +3/2 lines was duplicated by using linewidths of .346 and .410 gauss, respectively. A correction for the ^{10}B species was included, but the computer program used has no provision for second order shifts. The degree of fit presently attained is probably not yet optimized but is good enough to identify the splitting assignments beyond any doubt and to show that the three rings are equivalent or nearly equivalent on the esr time scale.

Dynamic Effects on the Triphenylboron Spectrum

The line-width variations in the triphenylboron spectrum contain information about the rate of motions of the radical or its individual phenyl groups. In principle, it should be possible to deduce the sign of a_B from the fact that the high-field lines are broader than those at low-field.[4] In practice, this would require dubious assumptions about the anisotropy of the g-tensor and the influence of spin density on the adjacent carbon atoms.

In the case of the triphenylmethyl radical[9] and the triphenylaminium ion-radical[10] the necessary assumptions are more justifiable. The splitting factors obtained for triphenylmethyl by means of ENDOR[5] and ESR[5,6,7,8] are a_{o-H} = 2.609, a_{m-H} = 1.143 and a_{p-H} = 2.857 gauss[5] and a_{oH} = 2.53, a_{m-H} = 1.11, a_{p-H} = 2.77, and $a_{C^{13}}$ = 26 gauss.[8] The high-field lines of the C^{13} triphenylmethyl spectrum are broader

than the low-field lines, indicating that the C^{13} splitting constant is positive.[8,9]

The hyperfine constants for triphenylaminium cation radical[10] are a_{o-H} 2.28, a_{m-H} 1.22, a_{p-H} 3.32, and $a_{N^{14}}$ 10.16. Again, the high-field lines are broader than the low-field lines and a_N is deduced to be positive.

The line width asymmetry between high and low fields in the spectra of the triphenylboron and related radicals is probably due to modulation of the anisotropic g tensor and electron-spin-nuclear spin dipolar interaction caused by Brownian motion.[4] Although the assumptions about the g-tensor are less justified because planar aromatic hydrocarbon anion radicals may not be as good models for the triphenylboron radical as for the others, it is probable that a_B is positive in triphenylboron anion radical. On the other hand a_B in trimesityl boron is believed to be negative.[1] This difference may reflect the greater deviation from coplanarity in trimesitylboron.

The difference in line-width between the $\widetilde{m}_B = +1/2$ and $\widetilde{m}_B = +3/2$ lines could be the result either of the Brownian motion of the molecule or of some process that modulates the hyperfine constants, for example a libration of the rings or a motion of solvent molecules o gegenions. While we are unable to identify this process completely, the fact that the effect is smaller in trimesitylboron anion radical even though a_B is greater (10.2 gauss) suggests that it is not Brownian motion. An attempt to improve resolution by either raising or lowering the temperature showed that the best resolution was obtained near room temperature. This suggests

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modulation due to variable solvation superimposed on that due to
Brownian motion: the contribution due to Brownian motion should
decrease at higher temperatures while a solvation effect might well
behave in the opposite way.

Other Tri-substituted Boron ESR Spectra

We have also briefly examined the esr spectra from the
reaction of several other triarylborons with alkali metals in DME.

Tris-p(tolyl)boron gave a spectrum resembling that of tri-
phenylboron, but no detailed analysis was made. Tris-(2,4,6-tri-
methyl-3,5-dinitrophenyl)boron[11] gave an initial spectrum consisting
of three broad lines, 1:2.5:1 with a 20 gauss splitting; this was
succeeded by the spectrum of dinitromesitylene anion radical.[12]
Tris-(p-dimethylaminophenyl)boron[13,14] gave a spectrum consisting
of four broad lines with further incompletely resolved fine structure
and a main 8.2 gauss spacing attributable to the boron anion radical;
the signal changed on standing and will be discussed further in a
later section.

Tris-(p-chlorophenyl)boron gave a signal completely identical
to that from unsubstituted triphenylboron. This surprising result
means that the replacement of chlorine atoms by hydrogen is much
faster than the cleavage of the triarylboron. The final spectrum
was that of diphenyl anion radical, the main cleavage product of
triphenylboron. However, p,p'-dichlorobiphenyl is rapidly reduced
to biphenyl under the same conditions.[17]

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Tris-(p-methoxyphenyl)boron[14,15] also gave a four line ^{11}B signal of about 8.1 gauss splitting. It had some partly resolved proton fine structure, more nearly resolved in the $\widetilde{m}_B$ = ±1/2 groups than in the $\widetilde{m}_B$ = ±3/2 groups.

Triethylboron and tri-n-propylboron failed to give ESR signals on treatment with Na/K in DME, although the metal was consumed. Tribenzylboron[15] reacted with Na/K in DME to give a dark green solution whose esr signal consisted of a single broad line extending over about 30 gauss. Tris(cyclohexyl)boron gave only a very weak and unstable signal.

Reductive Cleavage of Triarylborons

The reaction of triarylborons with alkali metals gives an anion radical which is stable indefinitely in some cases,[1] but which in other cases is subject to a cleavage reaction (1) of unknown mechanism.[1,2] An alternative reaction (2) has been observed only in the case of triphenylboron and tris-(p-tolyl)boron.

$$Ar_3 B \; \overset{..}{\cdot} \qquad \longrightarrow \qquad ArH \qquad (1)$$

$$Ar_3 B \; \overset{o}{\cdot} \qquad \longrightarrow \qquad Ar\text{-}Ar \qquad (2)$$

The stable anion radicals are those that are both sterically hindered and without strongly electron-attracting substituents. For example, the anion radical from trimesitylboron is stable, contrary

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to our earlier report.[2,16]   On the other hand we find that tris-
(2,4,6-trimethyl-3,5-dinitrophenyl)boron cleaves rapidly to give
the well-known esr signal of the dinitromesitylene anion radical,[12]
and the less hindered tris(2,4-dimethylphenyl)boron cleaves to give
unknown products but probably also by a type -1 reaction.[10]

Compounds known to cleave by reaction (1) are tris(o-xenyl)-
boron,[1a] and tris(α-naphthyl)boron.[1a]

Tris-(p-dimethylaminophenyl)boron certainly does not cleave
by reaction (2) or the esr of the biphenyl would have been detected
on further exposure to the metal; possibly it cleaves according to
reaction (1) which would give a product that would not give an esr
signal with alkali metal at room temperature in DME.   Reaction (1)
should be accompanied by the formation of some other boron species.
On further treatment of tris(p-dimethylaminophenyl)boron with Na/K
in DME the original 4-line signal, a_B = 8.3 gauss, is replaced by a
signal consisting of seven broad lines of relative intensities
1:2:3:4:3:2:1 at intervals of 3.1 gauss; it regenerates the original
four-line signal on standing.   This is definitely not a biphenyl
anion signal.   A species with strong interactions from two equivalent
boron nuclei might be expected to give a seven-line signal with
these relative intensities.

The reaction of tris(p-methoxyphenyl)boron[14] with Li in DME
gives a four line signal that decays on further reaction to a weaker
and narrower signal.   It does not give the easily detected biphenyl
anion radical signal, even though control experiments with p,p'-di-
methoxybiphenyl show that this substance is reduced to biphenyl under

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oi.r conditions.[17] It has further been shown that anisole also gives biphenyl anion radical on reaction with Li in DME. Hence both reactions (1) and (2) are excluded for this triarylboron. Prolonged reaction gave a precipitate that was not further investigated.

The Triphenylboron Cleavage Reaction

The reaction of triphenylboron with alkali metals in DME first gives the esr signal of the triphenylboron anion radical and then that of the biphenyl anion radical. Since the methods of synthesis of the borane via Grignard reactions give biphenyl as a side product, we tested our triphenylboron for this impurity by thin-layer chromatography and by H_2O_2 oxidation of the triphenylboron followed by an alkali metal esr test for biphenyl. These tests, the latter one very sensitive, failed to show any biphenyl impurity in our triphenylboron. The oxidation was necessary because triphenylboron in DME has a greater electron affinity than biphenyl and esr signal from triphenylboron containing a small amount of added biphenyl is just that of the triphenylboron anion radical.

Cleavage by reaction (1), leading to benzene, is a very minor process. Benzene was shown to be a product by examining the u.v. spectrum of the distillate from the cleavage reaction. However, the yield of benzene as determined by vapor phase chromatography and spectroscopy is less than 2%. The boron-containing products of the cleavage reaction are presumed to be derivatives of phenylboronic acid.[a] The possibility of intermediates containing two boron atoms

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[a] A nearly quantitative yield of phenylboronic anhydride was obtained from an experiment with diphenylboron chloride and Na/K in DME. Diphenylboron chloride in DME disproportionates and gives the $\phi_3 B^{\pm}$ esr signal followed by a $\phi_2^{\pm}$ esr signal.

will be discussed in a later section.

The biphenyls formed by the reaction of tris-(p-tolyl)boron or deuterium-labeled triphenylboron are bonded at the same carbon that was initially bonded to boron. Thus the product from tris-(p-tolyl)boron is p,p'-dimethylbiphenyl, and that from tris-(p-deuterophenyl)boron is p,p'-dideuterobiphenyl. More significant is the fact that the reaction is entirely intramolecular, both moieties of the biphenyl having come from the same triphenylboron molecule. This was demonstrated by an experiment in which a mixture of equal amounts of tris-(p-deuterophenyl)boron and tris-(3,5-dideuterophenyl) boron was treated with Li in DME. The signal from the mixture of triarylboron anion radicals was succeeded by an esr signal from a mixture of deuterated biphenyls. The esr spectrum matches that plotted by the computer for an equal mixture of the two symmetrical biphenyls using experimentally determined splitting constants. This is a good test for the absence of unsymmetrical biphenyl because that species should have a peak in a region where there is no interference from the two symmetrical biphenyls.

There are two precedents for the intramolecular formation of biaryls from arylboron compounds. One is the formation of di-α-naphthyl in good yield from the photolysis of tris(α-naphthyl)boron in CCl_4.[18] Experiments with bis-(α-naphthoyl) peroxide have shown that free α-naphthyl radicals are almost entirely converted to α-chloronaphthalene, and hence can not be intermediates in the formation of binaphthyl. The other example is the exclusive formation of symmetrical biphenyl by the electrode oxidation of a mixture of
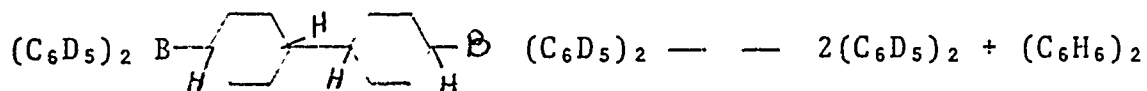
labeled and unlabeled tetraphenylborate ion, with benzene as a byproduct.[19]

Biphenyl has also been observed as a product of the reduction of triphenylamine,[20] and triphenylphosphine,[21] and in the mass spectra of triarylcarbinols.[22] Substituent effects in the latter reaction suggested an attack by a radical site on one aryl group on the polarizable π electrons of the other aryl group, with elimination of the bridging moiety.

Possible Diboron Compounds. — The reaction of tris-(p-dimethylaminophenyl)boron with Li in DME gave only the four-line boron radical signal, a_B = 8.3 gauss, with no resolved proton or nitrogen hyperfine structure. This signal gradually decayed on prolonged reaction with Li. A similar experiment with Na/K, however, gave different results: After about fifteen minutes the four-line boron signal was succeeded by a seven line signal, 1:2:3:4:3:2:1 relative intensities, with a 3.1 gauss interval. This is the spectrum to be expected if the signal is split by two equivalent boron atoms.

A partly resolved signal with seven lines at about 2.8 gauss intervals was obtained by treating perdeutero diphenylboron chloride with alkali metal in DME. A better signal with seven lines matching the expected intensities for the two-boron model (including a B^{10} correction) was obtained by carrying out the initial reaction in benzene at room temperature, then changing the solvent to DME. The interval between the lines in this signal was 2.93 gauss.

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Further reaction of this material with sodium-potassium alloy and DME caused the disappearance of the seven-line signal and its replacement by a four-line signal very much like that obtained from the reaction of perdeutero triphenylboron, $a_B = 8.3$ gauss, and no additional hyperfine structure. Still further exposure to alkali metal produced a signal attributable to a mixture of biphenyl and perdeutero biphenyl. This signal was reproduced precisely by computer simulation assuming a biphenyl perdeutero biphenyl ratio of 0.5 and including none of the unsymmetrical pentadeutero biphenyl. It should be noted that the unsymmetrical pentadeutero biphenyl would have been readily detected. This result shows that diphenylboron chloride does not form a radical that attacks benzene to give triphenylboron, since this would have given some of the unsymmetrical biphenyl. To explain the 2:1 ratio of products, it is necessary to assume that each $(C_6D_5)_2BCl$ gives rise to 1/2 of a biphenyl precursor. A further restriction is that the presumed two-boron species must not contain any protons in positions that would give rise to large proton coupling constants. This rules out structures such as I for the species with the 7-line signal.

$$(C_6D_5)_2 \; B \underbrace{}_{H} \underbrace{}_{H} \overset{H}{\underset{H}{}} \underbrace{}_{H} B \; (C_6D_5)_2 \; \text{---} \; \text{---} \; 2(C_6D_5)_2 \; + \; (C_6H_6)_2$$

I

However, it is necessary for the intermediate formed during the reaction in benzene to incorporate benzene in some way before the

solvent is replaced by DME. ·

In a search for boron compounds incorporating benzene we carried out the room-temperature reaction of diphenylboron chloride with Na/K in benzene for longer reaction times and without replacing the solvent with DME. A two-day reaction period gave a small amount of diphenylboronic acid in work-up. Longer reaction times gave a pyrophoric black precipitate containing all of the boron, leaving no boron compounds in the benzene. The reaction of diphenylboron chloride with Na/K in cyclohexane also gave a black pyrophoric precipitate. The solvent contained a compound with uv, nmr, and ir spectra resembling those of triphenylboron, but a pure sample was not obtained. Somewhat similar experiments by Auten and Kraus[23] with di-n-butylboron chloride and potassium in ether gave tributylboron and potassium di-n-butylboride. Kuchen and Brinkmann[24] obtained a pyrophoric solid of composition (C_6H_5B) by heating phenylboron dichloride.

One rationalization of the reaction of perdeutero diphenylboron chloride with Na/K in benzene, then in DME, is that the benzene stage of the reaction produces a $(C_6D_5)_2BM$-benzene adduct which on transfer to DME and further reaction gives $(C_6H_5)_2$ plus $(C_6D_5)_2\overset{..}{B}\text{-}B(C_6D_5)_2$, responsible for the seven-line signal. Further reduction of this diboron species in DME then gives $(C_6D_5)_2\overset{..}{B}:OR_2$, for the renewed four-line signal, and finally $(C_6D_5)_2$.

Attempts to stabilize boron radical intermediates as perdeuteropyridine or pyridine adducts as reported by Köster[25] gave only γ-dipyridyl esr signals.

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Disproportionation Reactions of Arylboron Compounds

Treatment of compounds of the type Ar_2BX with alkali metals in DME gives the esr spectrum of the corresponding $Ar_3B^{\cdot-}$; this is usually the first resolved signal seen, except in the case of diphenylboron chloride which gave a seven-line signal first. Examples are diphenylboron chloride, dimesitylboron fluoride,[16] and diphenyl boronic anhydride.

The signals from phenylboronic anhydride and phenylboron dichloride were unresolved.

The work on organo-boron chemistry is being prepared for publication in a journal.

References for Part E of Report

(1a) H. van Willigen, Dissertation, Amsterdam, 1965.

(1b) S.I. Weissman and H. van Willigen, J. Am. Chem. Soc., 87, 2285 (1965).

(2) J.E. Leffler, E. Dolan and T. Tanigaki, J. Am. Chem. Soc., 87, 927 (1965).

(3) E.W. Stone and A.H. Maki, J. Chem. Phys., 38, 1999 (1963).

(4a) J.H. Freed and G.K. Fraenkel, J. Chem. Phys., 39, 326 (1963).

(4b) R. Wilson and D. Kivelson, J. Chem. Phys., 44, 154 (1966).

(5) A.H. Maki, R.D. Allendoerfer, J.C. Danner and R.T. Keys, J. Am. Chem. Soc., 90, 4225 (1968).

(6) D.B. Chessnut and G.J. Sloan, J. Chem. Phys., 33, 637 (1960).

(7) JS. Hyde, J. Chem. Phys., 43, 1806 (1965).

(8) J. Sinclair and D. Kivelson, J. Am. Chem. Soc., 90, 5074 (1968).

(9) H. van Willigen and S.I. Weissman, J. Chem. Phys., 44, 420 (1966).

(10a) H. van Willigen, J. Am. Chem. Soc., 89, 2229 (1967).

(10b) R.I. Walter, ibid., 88, 1923 (1966).

(10c) E.T. Seo, R.F. Nelson, J.M. Fritsch, L.S. Marcoux, D.W. Leedy, and R.N. Adams, ibid., 88, 3498 (1966).

(11) R.T. Hawkins, Dissertation, University of Illinois, 1959.

(12) R.D. Allendoerfer and P.H. Rieger, J. Am. Chem. Soc., 88, 3711 (1966).

(13) G. Wittig and W. Herwig, Ber., 88, 962 (1955).

(14) D.S. Miller, Thesis, Florida State University, 1969.

(15) E. Krause and P. Nobbe, Ber., 63, 934 (1930).

(16)　On treatment of dimesitylboron fluoride with alkali metal in DME, a rapid disproportionation reaction causes the appearance of the esr signal of Mes_3B , mis-labeled $Mes_2B^\bullet$ in reference 2. The spectrum attributed to a Mes_2B pyridine complex was due to an adventitious inquirity from our oxygen-removal train.

(17)　R.E. Schwerzel, this laboratory.

(18a)　B.G. Ramsey, Dissertation, Florida State University, 1962.

(18b)　See also J.L.R. Williams, P.J. Grisdale, and J.C. Doty, J. Am. Chem. Soc., 89, 4538 (1967).

(19)　D.H. Geske, J. Phys. Chem., 66, 1743 (1962).

(20a)　M. Iwaizumi and T. Isobe, Bull. Chem. Soc. Japan, 38, 501 ((1965).

(20b)　A.D. Britt, M.M. Urberg and E.T. Kaiser, J. Org. Chem., 31, 1661 (1966).

(21)　A.D. Britt and E.T. Kaiser, J. Chem. Phys., 69, 2775 (1965).

(22)　F.W. McLafferty, G.E. van Lear and R. Kornfeld, J. Am. Chem. Soc., 90, 6240 (1968).

(23)　R.W. Auten and C.A. Kraus, J. Am. Chem. Soc., 74, 3398 (1952).

(24)　W. Kuchen and R-D. Brinkmann, Z. für anorganische u. allg. Chemie, 325, 225 (1963).

(25)　R. Köster, H. Bellut and E. Ziegler, Ang. Chem., 79, 243 (1967).

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
	Unclassified
	2b. GROUP
Florida State University.	NA

3. REPORT TITLE

Reactions of Free Radicals

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report: 1 July 1962 - 31 August 1967

5. AUTHOR(S) *(First name, middle initial, last name)*

John E. Leffler

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
28 August 1969	16	25

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-ARO-D-31-124-G730	
b. PROJECT NO.	NA
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	3605.4-C

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	U.S. Army Research Office-Durham Box CM, Duke Station Durham, North Carolina 27706

13. ABSTRACT

Results of research on the cleavage of triptycene and quinolizinium ions by alkali metals, and on the decomposition of substituted benzoyl peroxides and of cumyl peracetate are reported briefly. The esr spectra of a series of triarylboron anion radicals show selective line broadening effects. The cleavage of triphenylboron by alkali metals in DME has been shown to give biphenyl in boron molecule. Several reactions of diarylboron derivatives with alkali metals are also discussed.

14. KEY WORDS

Free radicals
chemical reactions
alkali metals
Cleavage
decomposition reactions

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